Chapter 7: Properties of Real Gases

Properties of Real Gases

Ideal gases:
- molecules have no intrinsic volume
- molecules do not interact

This works pretty well at:
- Low pressures
- Low densities
- High temperature (kinetic energy dominates)

\[ n_iRT = P_iV \] for each component in gas
\[ n_{total}RT = P_{total}V \]
\[ P_i = x_iP_{total} \]

\[ \rightarrow \] established experimentally

\[ \rightarrow \] Today we derive this from statistical mechanics (particle in box)

Van der Waals: \[ P = \frac{nRT}{V - nb} - a\frac{n^2}{V^2} \]
Redlich-Kwong: \[ P = \frac{nRT}{V-nb} - \frac{n^2a}{\sqrt{T}} \left( V+nb \right) \]

Virial equation of State (systematic)
\[ P = RT \left( \frac{1}{V_m} + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \ldots \right) \quad V_m = \frac{V}{n} \]

\[ B(T) : \text{power series in } T \]

for a range of volumes (condensation), pressure is the same
\[ \rightarrow \text{no way to fit against analytical function} \]

Ideal gas: cannot capture gas \[ \rightarrow \text{liquid transition} \]

\[ \rightarrow \text{Van der Waals} \]

\[ P = \frac{nRT}{V-nb} - a \frac{n^2}{V^2} \]
\[ P(V-nb)V^2 = nRTV^2 - an^2(V-nb) \]
\[ PV^3 - PnbV^2 = nRTV^2 - an^2V + an^2b = 0 \]

\[ \rightarrow \text{solve cubic equation for } V : \]
\[ x(x-1)(x+2) = 0 \quad x = 0, 1, -2 \]
\[ x(x^2+1) = 0 \quad x = 0, \pm i; \quad i^2 = -1 \]

From VDW cubic solution construct the flat region of graph
$\frac{\partial P}{\partial V} = 0$

Start to get one solution

$\frac{\partial P}{\partial V} = \frac{\partial^2 P}{\partial V^2} = 0$

$\rightarrow T_c$ at which

$\left( \frac{\partial P}{\partial V} \right)_{T_c} = \left( \frac{\partial^2 P}{\partial V^2} \right)_{T_c} = 0$

Do the calculation:

$T_c = \frac{8a}{27Rb}$

$a, b$ are VDW parameters

$P_c = \frac{a}{27b^2}$

$V_{m,c} = 3b$

What if $T > T_c$?

Increase density, but all in one supercritical phase (no phase transition)
**Compression Factor Z**

\[
Z = \frac{V_m^{\text{actual}}}{V_m^{\text{ideal}}} = \frac{PV_m}{RT}
\]

\[
V_m = \frac{V}{n}
\]

\[
V_m^{\text{ideal}} = \frac{RT}{P}
\]

Z : tabulated for many gases

Low \( T \), low \( P \), \( Z < 1 \), \( V_m < V_m^{\text{ideal}} \) → attraction dominates

High \( T \), (very) high \( P \), \( Z > 1 \), \( V_m > V_m^{\text{ideal}} \) → finite volume term dominates

**Law of Corresponding State**

-reduced, dimensionless variables

\[
T_r = \frac{T}{T_c}, \quad P_r = \frac{P}{P_c}, \quad V_{m,r} = \frac{V_m}{V_m^{c}}
\]

\( T_c, P_c, V_{m,c} \) = parameters for specific gas

Van der Waals has a unique form:

\[
P_r = \frac{8T_r}{3V_{m,r} - 1} - \frac{3}{V_{m,r}^2} \quad \rightarrow \text{same for every gas}
\]

\[
T_c = \frac{8a}{27bR}, \quad P_c = \frac{a}{27b^2}, \quad V_{m,c} = 3b
\]

\( a, b \) = VDW parameters

For any gas: Plot \( Z = \frac{V_m^{\text{actual}}}{V_m^{\text{ideal}}} \) vs \( T_r, P_r \)

→ virtually the same plot for any gas (not exactly)

→ know \( T_c, P_c \) for gas, use numerical curve to get \( V_{m,c} \) (figure 7.8 in book)

Example:

1.00 kg of \( CH_4 \) at \( T = 200 \) K, \( P = 68 \), \( V = ? \)
n = \frac{1 \text{ kg}}{16.09 \cdot 10^{-3} \text{ kg mol}^{-1}}

V_m^{\text{ideal}} = \frac{nRT}{P} = 17.52 \text{ L}

Table 7.2 in book \( CH_4 \rightarrow T_c = 190.56 \text{ K} \), \( P_c = 45.99 \text{ bar} \)

\( T_r = \frac{T}{T_c} = 1.21 \quad P_r = \frac{P}{P_c} = 1.48 \)

\( \rightarrow \) look at figure 7.8 \( Z(T_r, P_r) \approx 0.63 \)

\( V = ZV_m^{\text{ideal}} = 0.63 \cdot 17.52 \text{ L} = 11.04 \text{ L} \)

Two gases with the same \( T_r, P_r \rightarrow \) have the same \( V_{m,r} \)

**Fugacities** (pure substances)

For ideal gases \( \mu(T, P) = \mu^o(T) + RT \ln \left( \frac{P}{P_o} \right) \), where \( \mu^o \) is for the pure substance at pressure \( P_o = 1 \text{ bar} \). This is not really correct

\[
d\mu = V_m dP \quad \text{(constant } T \text{ )}
\]

\[
V_m^{\text{ideal}} = \frac{RT}{P}
\]

\[
d\mu = \frac{RT}{P} dP
\]

\[
\int_{P_o}^{P} d\mu = RT \int_{P_o}^{P} dP = RT \ln \left( \frac{P}{P_o} \right)
\]

Real gases

\[
V_m = ZV_m^{\text{ideal}}
\]

\[
= V_m^{\text{ideal}} + (Z-1)V_m^{\text{ideal}}
\]

\[
= \frac{RT}{P} + (Z-1)\frac{RT}{P}
\]

\[
\int_{P_o}^{P} d\mu = \int_{P_o}^{P} V_m dP = RT \int_{P_o}^{P} \frac{dP}{P} + RT \int_{P_o}^{P} (Z-1)\frac{RT}{P} dP
\]

\[
\mu = RT \ln \left( \frac{P}{P_o} \right) + RT \ln \gamma
\]

\( \gamma = \text{fugacity coefficient (calculated from integral)} \)
Fugacity: \[ f = \gamma p \]

\( f \) is like pressure, \( \gamma \) correction for non ideal gas behavior

\[
\mu(T, P) = \mu(T, P_o) + RT \ln \left( \frac{\gamma p}{P_o} \right)
\]

\[
= \mu(T, P_o) + RT \ln \left( \frac{f}{P_o} \right)
\]

Back to chemical equilibrium

\[
\left( \frac{\partial G}{\partial x} \right)_{T, P} = \sum \nu_i \mu_i(T, P)
\]

\[
= \Delta_f G_T^o + RT \ln \prod \left( \frac{f_i}{P_o} \right)^{\nu_i} \leftarrow K_f
\]

\[ 0 = \Delta_f G_T^o + RT \ln K_f \]

\[
= \Delta_f G_T^o + RT \ln \prod \left( \frac{f_i}{P_o} \right)^{\nu_i}
\]

\[
= \Delta_f G_T^o + RT \ln \prod \left( \gamma_P \frac{P}{P_o} \right)^{\nu_i} \leftarrow K_p
\]

\[
= \Delta_f G_T^o + RT \ln \prod \left( \gamma \right)^{\nu_i} + RT \ln \prod \left( \frac{P}{P_o} \right)^{\nu_i} + RT \ln \prod \left( \chi_i \right)^{\nu_i} \leftarrow K_x
\]

\[
K_f = K_p \cdot \prod \left( \gamma_i \right)^{\nu_i}
\]

\[
K_f = K_x \cdot \prod \left( \gamma_i \right)^{\nu_i} \left( \frac{P}{P_o} \right)^{\Delta p_{\text{env}}}
\]

\[
RT \ln K_f = -\Delta_f G_T^o \quad \text{Where } -\Delta_f G_T^o \text{ is found from } \Delta_f G
\]